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Supporting Information

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Supporting Information

C-H Bond Activation by [(diimine)$Pd^{II}(\mu_2\text{-}OH)]_2^{2+}$ Dimers: Mechanism- Guided Catalytic Improvement.

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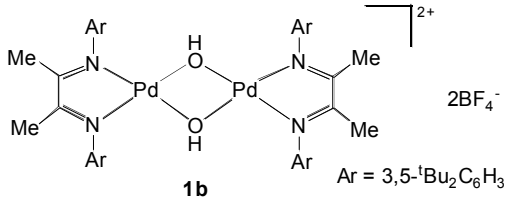
I. General methods

Unless otherwise noted all reagents were commercially obtained and used without further purification. The Pt hydroxy-bridged dimer $[(diimine)Pt(\mu\text{-}OH)]_2\cdot[BF_4]_2$ (**1a**),[1] Pd bis(aquo) dication $[(diimine)Pd(OH_2)_2]\cdot[BF_4]_2$ (**2b**)[2] and solutions of BF_3 in TFE[3] were synthesized using literature procedures. All reactions described were conducted under an atmosphere of air, and solvents were not dried prior to use unless otherwise noted. When used in anhydrous conditions, dichloromethane-d_2 (DCM-d_2) and dichloroethane-d_4 (DCE-d_4) were prepared by vacuum transfer from a suspension of CaH_2 and filtration through a syringe filter to remove particulate residue. ^{1}H NMR spectra were recorded at ambient temperature using a Varian Mercury 300 MHz spectrometer, unless otherwise noted. The data are reported by chemical shift (ppm) from tetramethylsilane, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet; dd, double doublet; dt, double triplet), coupling constants (Hz), and integration. Mass spectra were acquired on a Finnigan LCQ ion trap or Agilent 5973 Network mass selective detector and were obtained by peak matching. UV/Vis absorbance spectra were recorded on an Agilent 8453 UV/Vis Spectrometer equipped with an HP 89090A Peltier temperature control. Kinetics for the reaction between $[(diimine)Pt(\mu\text{-}OH)]_2^{2+}$ (**1a**), indene and acid (either aqueous HBF_4 or BF_3 in TFE) were performed using an analogous procedure to that described previously for the reaction between **1a**, cyclohexene and acid.[1] These experiments indicated that these reactions appeared to follow the same pathway.

In the course of this work crystals of **2b** suitable for X-ray diffraction were grown from a saturated solution of CD_2Cl_2, (further information about the structure is given in Section VIII of the SI).

II. Experimental details for new compounds and synthetic procedures

1. Improved synthesis of palladium hydroxy-bridged dimer **1b**:

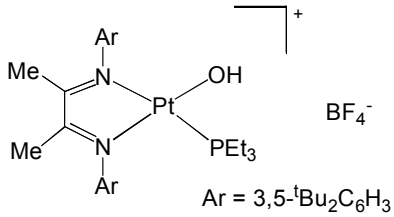


1b

$[(Diimine)Pd(OH_2)_2]^{2+}$ (**2b**, 75 mg, 0.10 mmol) and polymer-bound diethylamine[4], 1 % cross linked with divinylbenzene (1.5 mmol per g, 140 mg) were weighed out in an 20 mL vial with a stir bar. To these solids was added dichloromethane (15 mL, Omnisolv™) and the suspension was stirred for 45 minutes at room temperature. The resulting suspension, consisting of a brown solid in a yellow solution, was filtered to give a yellow solution. The filtrate was collected and the solvent removed *in vacuo*. The resulting residue was dissolved in 10 mL of dichloromethane and filtered to remove any residual solid supported base. The filtrate was collected and the solvent removed *in vacuo* to give **1b** as a yellow solid, 37 mg, 85%. Crystals of **1b** suitable for X-ray diffraction were grown from a saturated solution of CD_2Cl_2 (further information about the structure is given in Section VII of the SI).

The ^{1}H NMR data was consistent with that previously reported for **1b**.[1, 2]

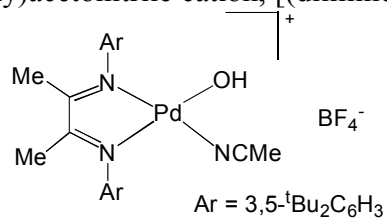
2. Synthesis of palladium(hydroxy)triethylphosphine cation, $[(diimine)Pt(OH)(PEt_3)]^+$:



In a nitrogen-filled glove box, triethylphosphine (1.9 μL, 12.9 μmol) was added via a microliter syringe to a J. Young NMR tube containing a dichloromethane-d_2 (~ 600 μL, anhydrous) solution of $[(diimine)Pd(\mu\text{-}OH)]_2^{2+}$ (**1b**, 10 mg, 6.6 μmol). The solution immediately changed from turbid yellow to a clear orange-red. The resulting solution contained ^{1}H NMR signals consistent with $[(diimine)Pt(OH)(PEt_3)]^+$; mass spectrometry also confirmed that a species consistent with this formula was present. Attempts to isolate this compound resulted in decomposition to multiple unknown products.

^{1}H NMR (300 MHz, dichloromethane-d_2, 21 °C) δ = 7.53 (t, ^4J(H,H) = 1.2 Hz, 1H), 7.49 (t, ^4J(H,H) = 1.2 Hz, 1H), 7.07 (d, ^4J(H,H) = 1.8 Hz, 2H) 6.90 (d, ^4J(H,H) = 1.8 Hz, 2H) 2.57 (s, 3H), 1.7 (s, 3H), 1.37 (s, 18H), 1.36 (s, 18H) 1.09-1.33 (m, 6H), 0.90-1.05 (m, 9H). ^{31}P NMR (121.368 MHz, dichloromethane-d_2, 21 °C) δ = 8.82 (t, J(P,Pt) = 1918). HRMS for $[C_{38}H_{48}PON_2Pt]^+$: calc'd 790.4430 g/mol, found 790.4404 g/mol.

3. Synthesis of palladium(hydroxy)acetonitrile cation, $[(diimine)Pd(OH)(MeCN)]^+$:

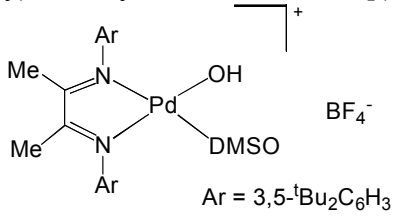


Acetonitrile (6.6 μL, 0.12 mmol) was added via a microliter syringe to an NMR tube containing a dichloromethane-d_2 (~600 μL, anhydrous) solution of $[(diimine)Pd(\mu\text{-}OH)]_2^{2+}$ (**1b**, 6.9 mg, 4.40 μmol). After 30 minutes the turbid yellow solution homogenized. After 24 hours the solution had turned a yellow-orange, and ^{1}H NMR revealed the presence of new resonances consistent with $[(diimine)Pd(OH)(MeCN)]^+$; mass spectrometry also confirmed that a species consistent with this formula was present. Attempts to isolate this compound resulted in decomposition to multiple unknown products.

^{1}H NMR (300 MHz, dichloromethane-d_2, 21 °C) δ = 7.29 (t, ^4J(H,H) = 1.7 Hz, 1H), 7.15 (t, ^4J(H,H) = 1.7 Hz, 1H), 6.90 (d, ^4J(H,H) = 1.7 Hz, 2H), 6.64 (d, ^4J(H,H) = 1.2 Hz, 2H), 1.24 (s, 18H), 1.17 (s, 18H), 6H from the methyl backbone of the ligand and 3H from acetonitrile obscured by solvent and impurities. MS (FAB$^+$) for $[C_{40}H_{51}ON_3Pd]^+$: $[M]^+$ = 625.2 m/z.

The solvent was removed under reduced pressure and the solids were dissolved in CD_2Cl_2. Indene (3.0 μL, 26 μmol) was added via syringe and the solution was heated for 24 hours at 40ºC. No change was observed so the solution was allowed to sit at room temperature. After 5 days the solution was darker and analysis by ^{1}H NMR revealed conversion to **4b**.

4. Synthesis of palladium(hydroxy)dimethylsulfoxide cation, $[(diimine)Pd(OH)(DMSO)]^+$:



Dimethylsulfoxide (12.0 μL, 0.160 mmol) was added via a microliter syringe to a J. Young NMR tube containing a dichloromethane-d_2 (~600 μL) solution of $[(diimine)Pd(OH_2)_2]^{2+}$ (**2b**, 5.3 mg, 3.94 μmol). After several hours the turbid yellow solution homogenized. After 24 hours the solution had turned a yellow-orange and ^{1}H NMR revealed the presence of new resonances consistent with $[(diimine)Pd(OH)(DMSO)]^+$; mass spectrometry also confirmed that a species consistent with this formula was present. Attempts to isolate this compound resulted in decomposition to multiple unknown products.

^{1}H NMR (300 MHz, dichloromethane-d_2, 21 °C) δ = 7.29 (t, ^4J(H,H) = 1.5 Hz, 1H), 7.15 (t, ^4J(H,H) = 1.5 Hz, 1H), 6.90 (d, ^4J(H,H) = 1.5 Hz, 2H), 6.58 (d, ^4J(H,H) = 1.5 Hz, 2H), 1.23 (s,

18H), 1.17 (s, 18H), 6H from methyl backbone of the ligand and 6H from DMSO were obscured by solvent and impurities. MS (FAB$^+$) for $[C_{41}H_{54}SO_2N_2Pd]^+$: $[M]^+$ = 661.4 m/z.

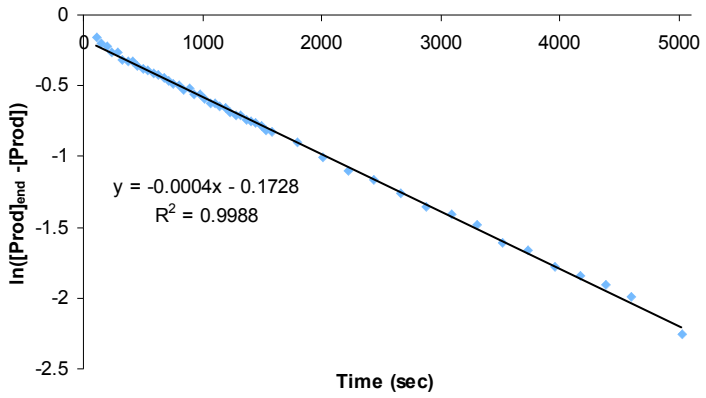
Indene (5.0 μL, 43 μmol) was added via syringe to the J. Young NMR tube and the solution was heated at 60ºC for 4 days. The solution darkened and analysis by ^{1}H NMR revealed complete conversion to **4b**.

III. Experimental procedure and kinetics data for reactions between [(diimine)Pd(OH$_2$)$_2$]$^{2+}$ (2b) and indene

For a standard kinetics experiment [(diimine)Pd(OH$_2$)$_2$]$^{2+}$ (**2b**, 10 mg, 0.01 mmol) was dissolved in 700 μL of 6:1 $C_2D_4Cl_2$:d_3-TFE in a J. Young NMR tube. Appropriate amounts of indene and/or BF_3 in TFE (0.56 M) were then added and the J. Young tube quickly placed into the NMR spectrometer, which had been preheated to 60 ºC. The growth of the product, **4b**, was monitored by integration of a series of ^{1}H NMR spectra recorded at different times. In all of these reactions some background polymerization of indene was observed, but this does not appear to have affected the kinetics of the reactions. The ^{1}H NMR spectrum of the reaction mixture at the end of the reaction was consistent with that previously reported for **4b**.[1] Several reactions were run in duplicate or triplicate to make sure that reactions were reproducible.

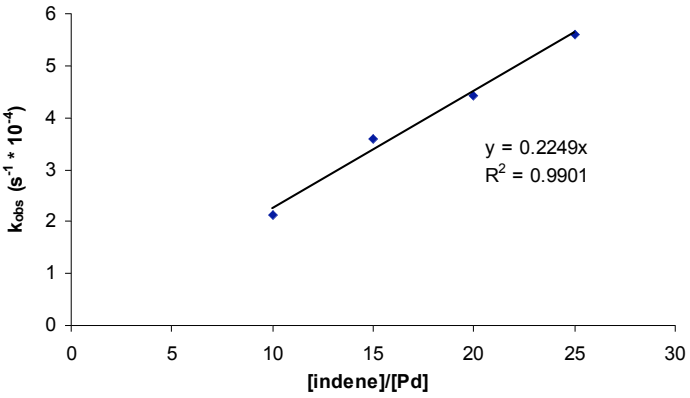
The first order dependence in [Pd] was established by performing a reaction with 20 equivalents of indene. The graph of ln([Prod]$_{end}$-[Prod]) (where [Prod] = [**4b**]) against time is linear up to approximately 3 half-lives, as shown in Figure S1, which is consistent with a first order dependence on [Pd].

Figure S1: Graph of ln([Prod]$_{end}$-[Prod]) against time for reaction between **2b** and 20 equivalents of indene at 60 ºC.



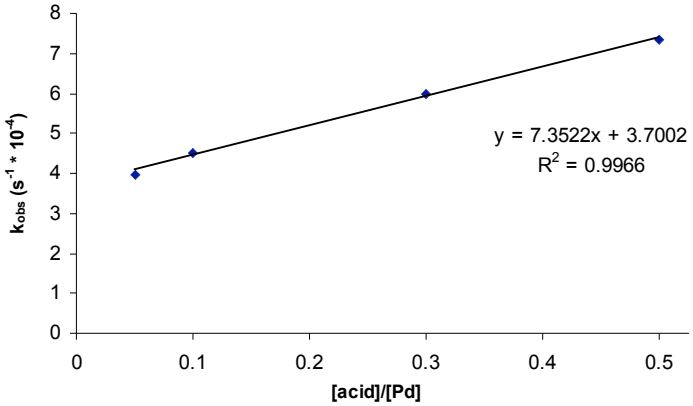
The order of the reaction in [indene] was determined by performing a series of reactions at different [indene] concentrations. k_{obs} was determined for each trial and the plot of k_{obs} vs. [indene] is shown in Figure S2. The linear nature of the plot indicates that the reaction is first order in [indene].

Figure S2: Graph of k_{obs} against [indene]/[Pd] for reaction between **2b** and indene at 60 ºC.



The order of the reaction in [BF_3] was determined by performing a series of reactions with 20 equivalents of indene at different [BF_3] concentrations. k_{obs} was determined for each trial and the plot of k_{obs} vs. [BF_3] is shown in Figure S3. Higher concentrations of BF_3 could not be used because they resulted in extremely fast polymerization of indene which interfered with the C-H activation reaction. The linear nature of the plot and non-zero intercept indicate a two-term rate law, in which one component is zero order and the other is first order in [BF_3]. Chemically, this could be explained by parallel steps for the displacement of coordinated water by indene, one acid-assisted and the other not. Similar behavior was previously observed for the related Pt system.[1]

Figure S3: Graph of k_{obs} against [BF_3]/[Pd] for reaction between **2b** and 20 equivalents of indene at 60 ºC.



The effect of water on the rate of reaction was determined by performing a series of reactions with 20 equivalents of indene at different water concentrations. D_2O was used as the water source to minimize interference in ^1H NMR spectra. k_{obs} was determined for each trial and the plot of k_{obs} vs. [water] is shown in Figure S4.

Figure S4: Graph of k_{obs} against [water]/[Pd] for reaction between **2b** and 20 equivalents of indene at 60 ºC.

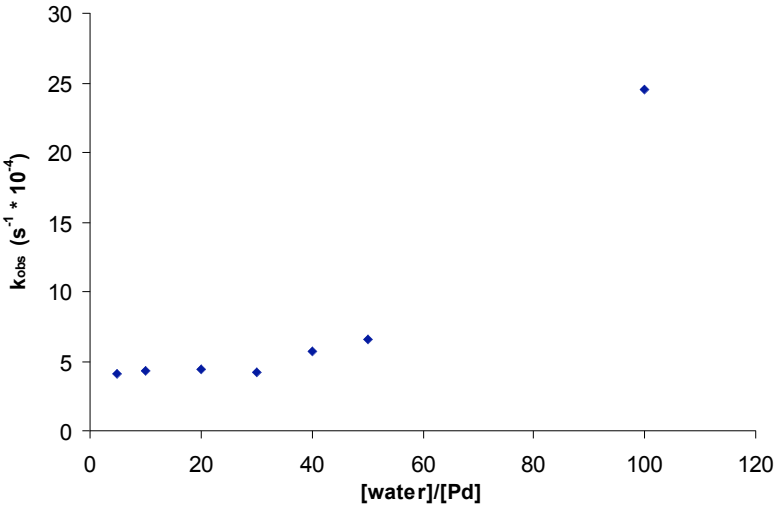
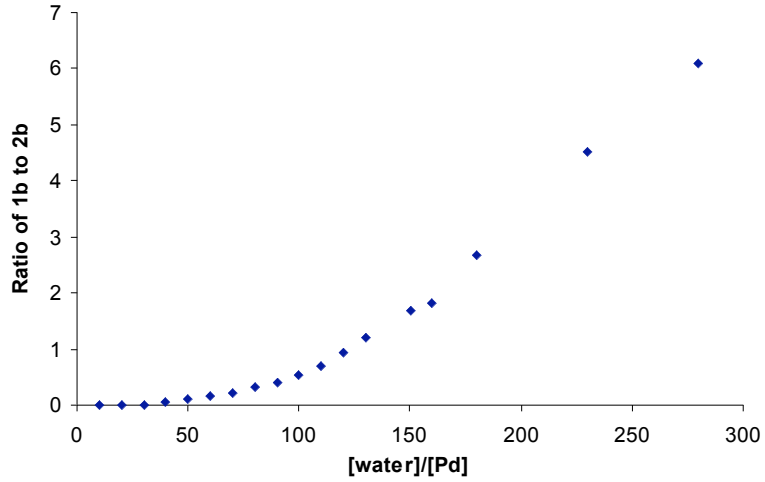
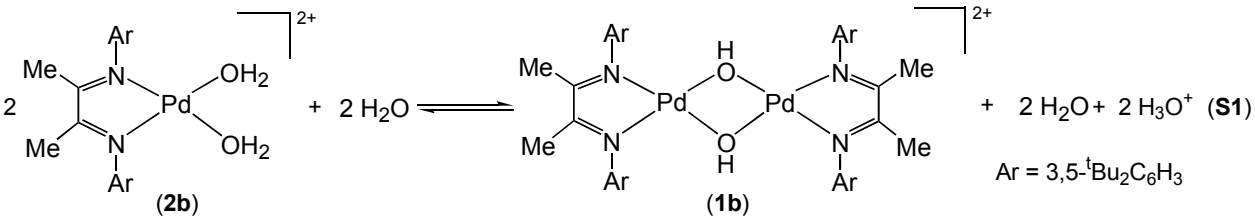


Figure S4 shows that at low [water] there is no effect on the rate of conversion of **2b** and indene into **4b**. However, at higher [water] there is a significant increase in rate. We believe that this increase is due to the conversion of **2b** into **1b**, which is more reactive with indene. An experiment was performed in which $[(diimine)Pd(OH_2)_2]^{2+}$ (**2b**, 10 mg, 0.01 mmol) was dissolved in 700 μL of 6:1 $C_2D_4Cl_2$:d_3-TFE in a J. Young NMR tube. Small aliquots of D_2O were then added to the NMR tube and the ^1H NMR spectrum recorded after each addition. Figure S5 demonstrates how the ratio of **2b** to **1b** changes as the [water] is increased. The reaction could not be run to completion because the reaction mixture phase-separated, indicating that the solution was saturated in water, before complete conversion of **2b** to **1b** had occurred.

Figure S5: Graph of ratio of **1b** to **2b** against [water]/[Pd] as D_2O is added to a solution of **2b** in 6:1 $C_2D_4Cl_2$:d_3-TFE.



Presumably water shifts the equilibrium from **2b** towards **1b** by diluting the acid present in solution and effectively lowering [H_3O^+]. A balanced equation for the reaction is shown below (Eq. S1).

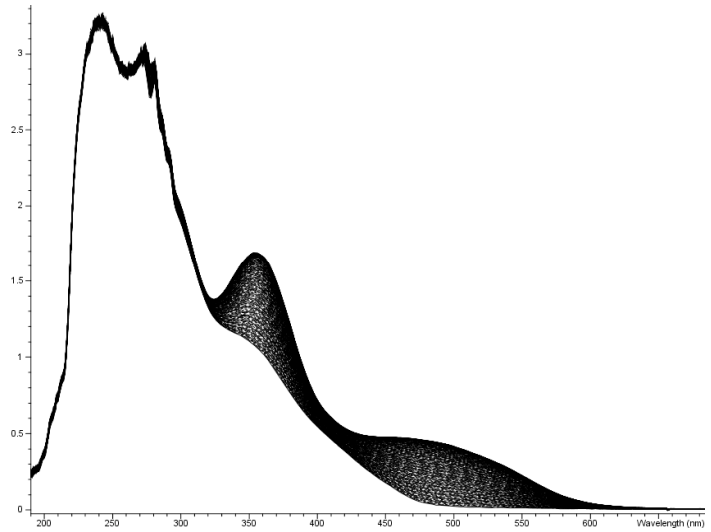


IV. Experimental procedure and kinetics data for reactions between [(diimine)Pd(μ-OH)]$_2^{2+}$ (1b) and indene

For a standard kinetics experiment, a stock solution of [(diimine)Pd(μ-OH)]$_2^{2+}$ (**1b**, 4 mg, 3.0 μmol) in 2 mL of CH_2Cl_2 was prepared. Two other stock solutions containing indene (88 μL, 0.75 mmol) and (44 μL, 0.38 mmol) in 10 mL CH_2Cl_2 were prepared. In order to carry out kinetics reactions, 125 μL of the Pd stock solution was added to a 1 mm quartz UV/Vis cuvette. The appropriate amount of the indene stock solution was then added and the total volume of the solution made up to 275 μL using a mixture of TFE (or MeOH) and CH_2Cl_2, depending on the amount of TFE required. UV/Vis spectra were acquired every 5 seconds at 25 ºC and the absorbance at 500 nm was monitored. This corresponded to monitoring the concentration of **4b** (product) in solution. The cuvette was inverted every 20 seconds to ensure adequate mixing and return any CH_2Cl_2 which had evaporated and condensed at the top of the cuvette to the main solution. The order in which reagents were added was shown to have no effect on the rate or kinetic profiles of the reaction.

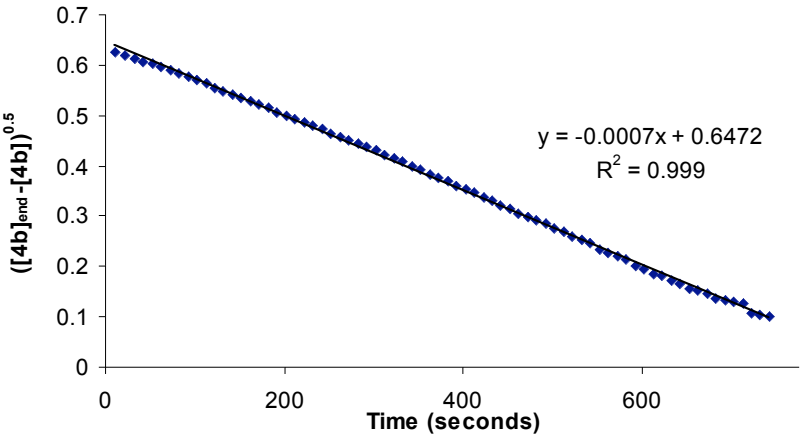
A representative time course UV/Vis spectra for the reaction of **1b** with indene is shown in Figure S6. The growth of the peak at 500 nm can be clearly seen.

Figure S6: Evolution over time of the UV/Vis spectrum for a solution of **1b** and indene in CH_2Cl_2/TFE.



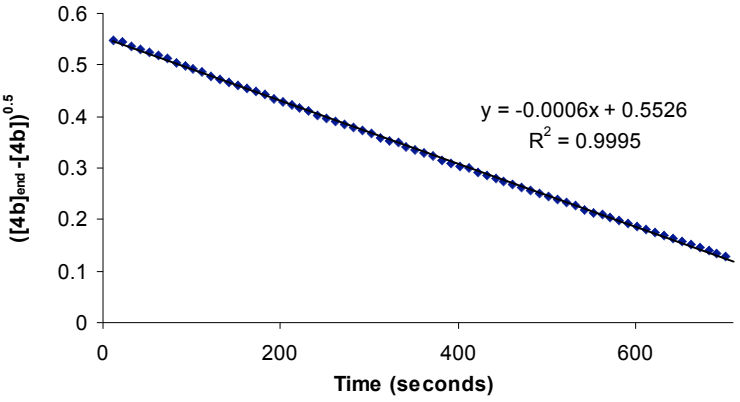
The half-order dependence in [Pd] was established by performing a reaction with 40 equivalents of indene and 675 equivalents of TFE. The graph of $([Prod]_{end} - [Prod])^{0.5}$ against time is linear up to approximately 3 half-lives, as shown in Figure S7, which is consistent with a half order dependence on [Pd].

Figure S7: Graph of $([Prod]_{end}\text{-}[Prod])^{0.5}$ against time during reaction between **1b** and 40 equivalents of indene in a 5.5:1 mixture of CH_2Cl_2:TFE (675 equivalents of TFE).



A similar half-order dependence on [Pd] was observed when MeOH was used as an additive. Figure S8 shows that the graph of $([Prod]_{end}\text{-}[Prod])^{0.5}$ against time is linear up to approximately 3 half-lives, when MeOH was used as the additive.

Figure S8: Graph of $([Prod]_{end}\text{-}[Prod])^{0.5}$ against time during reaction between **1b** and 40 equivalents of indene in a 4.5:1 mixture of CH_2Cl_2:MeOH (6630 equivalents of MeOH).



The order of the reaction in [indene] was determined by performing a series of reactions at different [indene] concentrations, with fixed concentrations of [TFE] or [MeOH]. k_{obs} was determined for each trial and the plot of k_{obs} vs. [indene] using TFE as an additive is shown in Figure S9, while the corresponding plot using MeOH as an additive is shown in Figure S10. The linear nature of the plots indicates that in both cases the reaction is first order in [indene].

Figure S9: Graph of k_{obs} against [indene]/[Pd] for reaction between **1b** and indene with 803 equivalents of TFE.

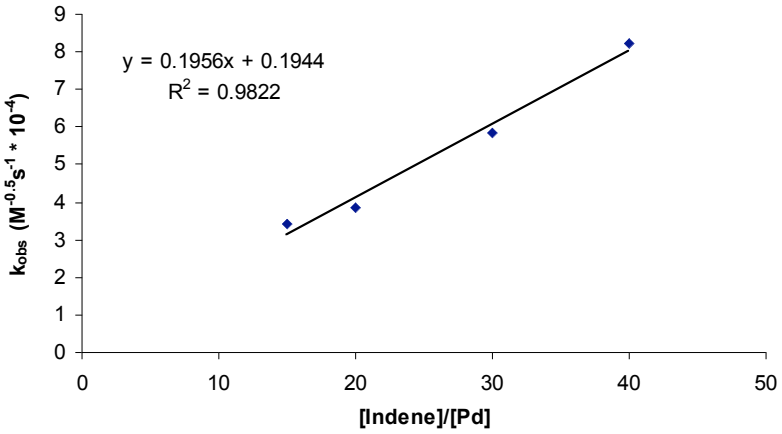
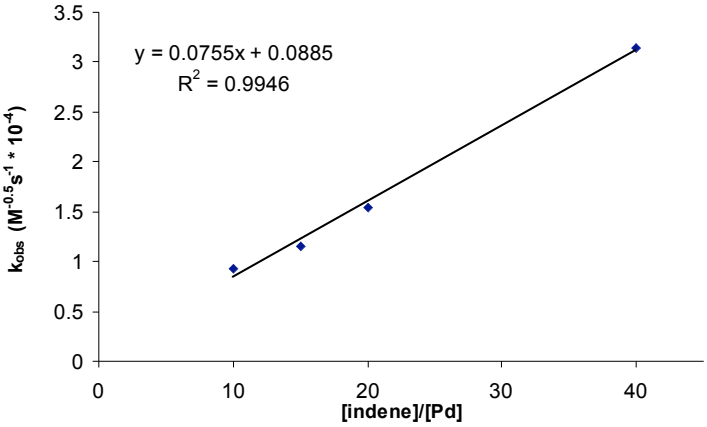


Figure S10: Graph of k_{obs} against [indene]/[Pd] for reaction between **1b** and indene with 6630 equivalents of MeOH.



The order of the reaction in [TFE] or [MeOH] was determined by performing a series of reactions with 40 equivalents of indene at different [TFE] or [MeOH] concentrations. k_{obs} was determined for each trial and the plot of k_{obs} vs. [TFE] is shown in Figure S11, while the corresponding plot of k_{obs} vs. [MeOH] is shown in Figure S12. The linear nature of the plots indicates that the reaction is first order in [MeOH] or [TFE]. A series of reactions (with a new stock solution), indicates that even when the reaction is performed at high concentrations of [TFE] the first order dependence holds. The non-zero intercept is indicative of a two-term rate law, in which one component is first order in [TFE] or [MeOH] and the other component is zero order in [TFE] or [MeOH]. The former is consistent with the proposed mechanism, in which the added alcohol serves to cleave the dimer and generate a species more reactive towards indene, while the latter suggests that there is a (slower) direct reaction of indene with the dimer. The intercepts for the two plots agree well within experimental accuracy, as they should.

Figure S11: Graph of k_{obs} against [TFE]/[Pd] for reaction between **1b** and 40 equivalents of indene.

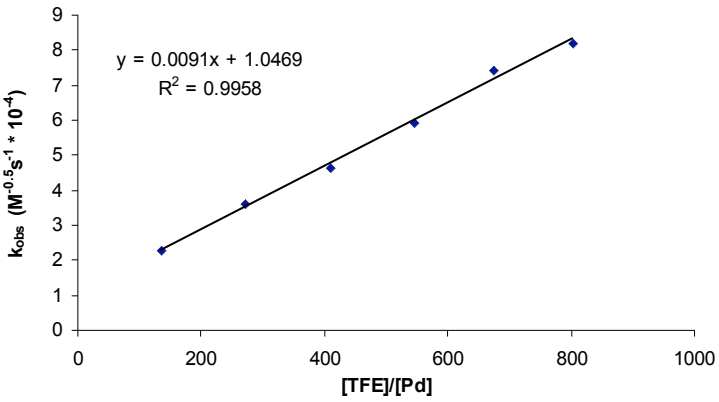
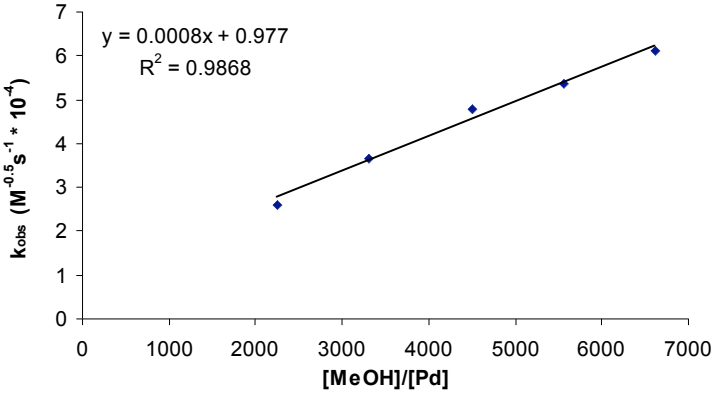


Figure S12: Graph of k_{obs} against [MeOH]/[Pd] for reaction between **1b** and 40 equivalents of indene.



A kinetic isotope effect (KIE) of 1.6(1) was measured by comparing the rates of three reactions using 1,1,3-trideuteroindene[5] with three reactions using indene. These reactions were performed using the procedure outlined above with 40 equivalents of indene and 803 equivalents of TFE.

V. Reactions between [(diimine)Pt(μ-OH)]$_2^{2+}$ (1a), [(diimine)Pd(μ-OH)]$_2^{2+}$ (1b) and HBF_4

We previously showed [(diimine)Pt(μ-OH)]$_2^{2+}$ (**1a**) and [(diimine)Pt$(OH_2)_2$]$^{2+}$ (**2a**) equilibrate slowly in the presence of added aqueous HBF_4.[1] These reactions were carried out using CD_2Cl_2 as the solvent. When [(diimine)Pd(μ-OH)]$_2^{2+}$ (**1b**) was treated with 3 equivalents of aqueous HBF_4 in CD_2Cl_2, a yellow solid precipitated out of solution. Addition of 50 μL of d_3-TFE led to the dissolution of the yellow solid and ^{1}H NMR indicated that only [(diimine)Pd$(OH_2)_2$]$^{2+}$ (**2b**) was present in solution. The insolubility of **2b** in CD_2Cl_2 presumably drives the reaction to completion and therefore this reaction cannot be used to estimate K_{eq}.

In order to obtain an estimate for the value of K_{eq} for the reaction between [(diimine)Pd(μ-OH)]$_2^{2+}$ (**1b**) and added aqueous HBF_4, the solvent was changed to a 6:1 mixture of CD_2Cl_2:d_3-TFE. In this solvent mixture both **1b** and **2b** are fully soluble. K_{eq} was determined from integrations of the aromatic peaks at room temperature using the formula $K_{eq} = [\mathbf{2b}]^2/([\mathbf{1b}]\cdot$

$[HBF_4]^2$) M^{-1}. When 3.62 equivalents of aqueous HBF_4 were added to **1b**, equilibration between **1b** and **2b** appeared to occur in minutes at room temperature and K_{eq} was 1217 M^{-1}. A comparison experiment was performed between $[(diimine)Pt(\mu\text{-}OH)]_2^{2+}$ (**1a**) and added aqueous HBF_4 in a 6:1 mixture of CD_2Cl_2:d_3-TFE. In this case the reaction was extremely slow, but after 72 hours only **2a** was observed in solution by ^1H NMR spectroscopy, so complete conversion of **1a** had occurred.

VI. Catalytic conversion of cyclohexene to benzene

Representative procedure for cyclohexene oxidation with **1b**:

1b (3.0 mg, 2.2 μmol) was weighed out in a J. Young NMR tube. TFE-d_4 (600 μL) and cyclohexene (16.2 mg, 197 μmol) were added, and the tube was degassed using three consecutive freeze-pump-thaw cycles. The reaction mixture was then placed under 1 atmosphere of O_2 and submerged in a 60 ^oC oil bath. The reaction was monitored at regular time intervals using ^1H NMR spectroscopy.

We have previously observed in the reaction of **2b** with cyclohexene under 1 atmosphere of O_2 that even after twelve hours no benzene (or cyclohexane) had formed and that the oxidation/disproportionation reactions did not appear to commence until after the mixture had been heated for approximately fifteen hours.[1] In the reactions of **1b** with cyclohexene, benzene was observed after two hours. After 24 hours using 1 mol % **1b** as the catalyst, 25 % of the cyclohexene had been converted to benzene, whereas the corresponding number using 5 mol % of **2b** was only 8 %. Conversion continued to occur after this time, but after 24 hours in the case of catalysis using **2b** the disproportionation of cyclohexene to benzene and cyclohexane also started to occur, which makes direct comparison difficult. A maximum conversion of 60 % after 3 days was reached using **1b** as a catalyst without the observation of any cyclohexane. Also, once conversion had stopped, presumably because of the complete consumption of O_2 which was the limiting reagent, a palladium mirror was coated on the walls of the NMR tube during catalysis with **2b**, while this was not the case for catalysis using **1b** and ^1H NMR spectroscopy indicated that at least some of **1b** catalyst was still intact. Taken together these results demonstrate that **1b** is a considerably more active and stable catalyst.

VII. X-ray structure determination for 1b

Crystallographic data for **2b** have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 692723.

Table S1. Crystal data and structure refinement for 1b.

Empirical formula	$[C_{64}H_{96}N_4O_2Pd_2]^{+2}\ 2[BF_4]^-$	
Formula weight	1339.87	
Crystallization Solvent	Dichloromethane	
Crystal Habit	Plate	
Crystal size	0.16 x 0.15 x 0.06 mm^3	
Crystal color	Yellow	

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9858 reflections used in lattice determination	2.45 to 29.88°	
Unit cell dimensions	a = 10.7826(5) Å b = 13.2100(5) Å c = 15.3994(7) Å	α= 108.315(2)° β= 94.061(2)° γ = 106.256(2)°
Volume	1968.52(15) $Å^3$	
Z	1	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.130 Mg/m^3	
F(000)	698	
θ range for data collection	1.71 to 29.88°	
Completeness to θ = 29.88°	98.8 %	
Index ranges	$-14 \le h \le 15, -18 \le k \le 18, -21 \le l \le 21$	
Data collection scan type	ω scans; 17 settings	
Reflections collected	53239	
Independent reflections	11235 [R_{int}= 0.0465]	
Absorption coefficient	0.512 mm^{-1}	
Absorption correction	None	
Max. and min. transmission	0.9699 and 0.9225	

Table S1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	11235 / 360 / 425
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	3.841
Final R indices [I>2σ(I), 8184 reflections]	R1 = 0.0661, *w*R2 = 0.1103
R indices (all data)	R1 = 0.0874, *w*R2 = 0.1112
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	2.030 and -1.600 e.Å^{-3}

Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

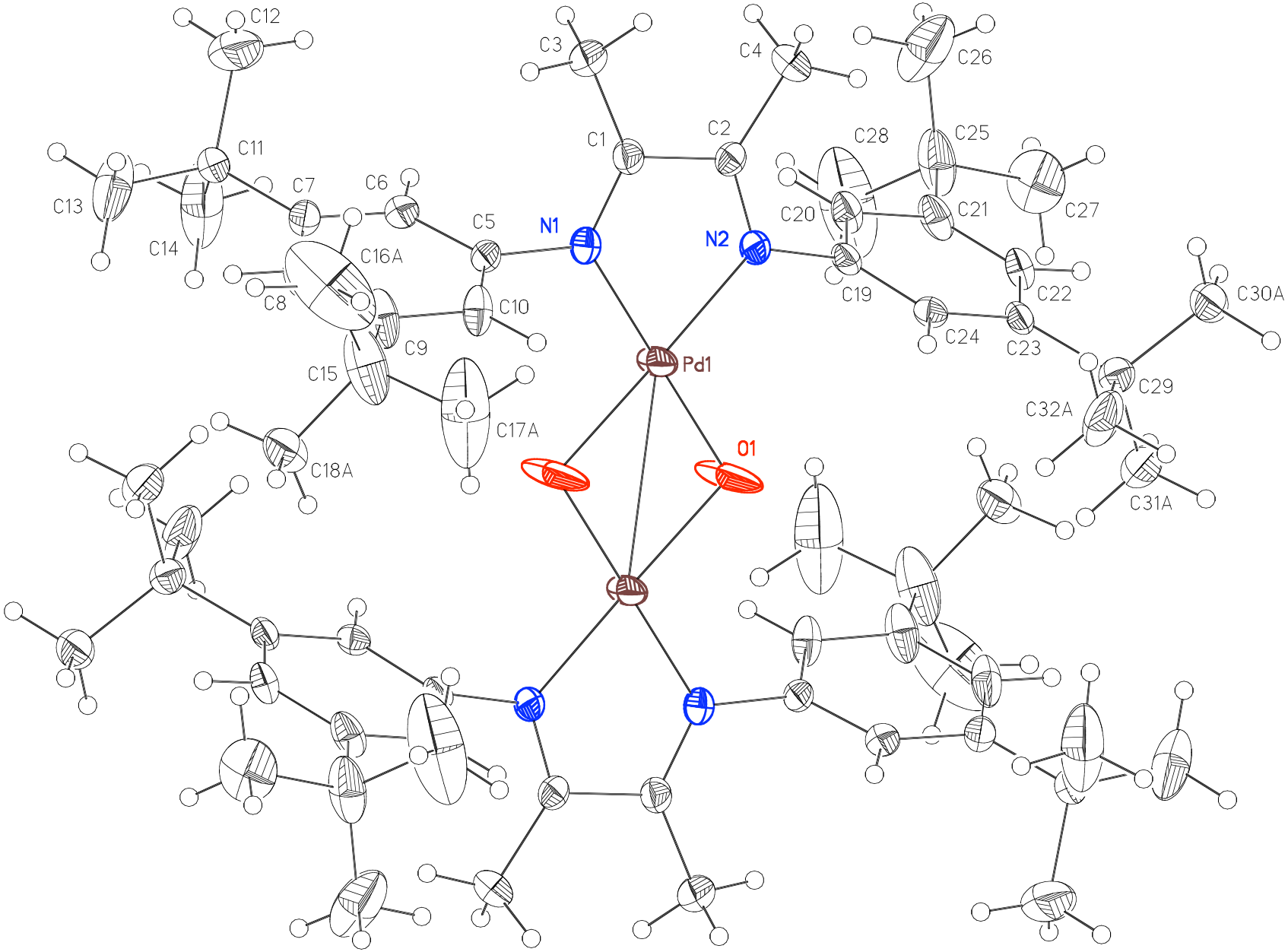
The crystals contain disordered solvent occupying 380.1 Å^3 (19.3% of total unit cell volume). Solvent flattening as implemented in SQUEEZE[1] was employed to account for the solvent area. A total of 154 electrons were recovered for the solvent area which is in very good agreement with four molecules of dichloromethane.

Additional disorder was observed in the tetrafluoroborate anion and in two of the tertiary butyl groups. This disorder was included in the model refinement with restraints on the distances and angles of the affected tertiary butyl groups (see Table 2 for occupancies).

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

[1] SQUEEZE - Sluis, P. v.d.; Spek, A. L. Acta Crystallogr., Sect A 1990, 46, 194-201.


C12
C3
C4
C26
C11
C1
C2
C28
C25
C13
C7
C6
C5
N1
N2
C20
C21
C27
C14
C16A
C8
C10
C19
C22
C30A
C9
C24
C23
Pd1
C15
C29
C32A
C17A
O1
C18A
C31A

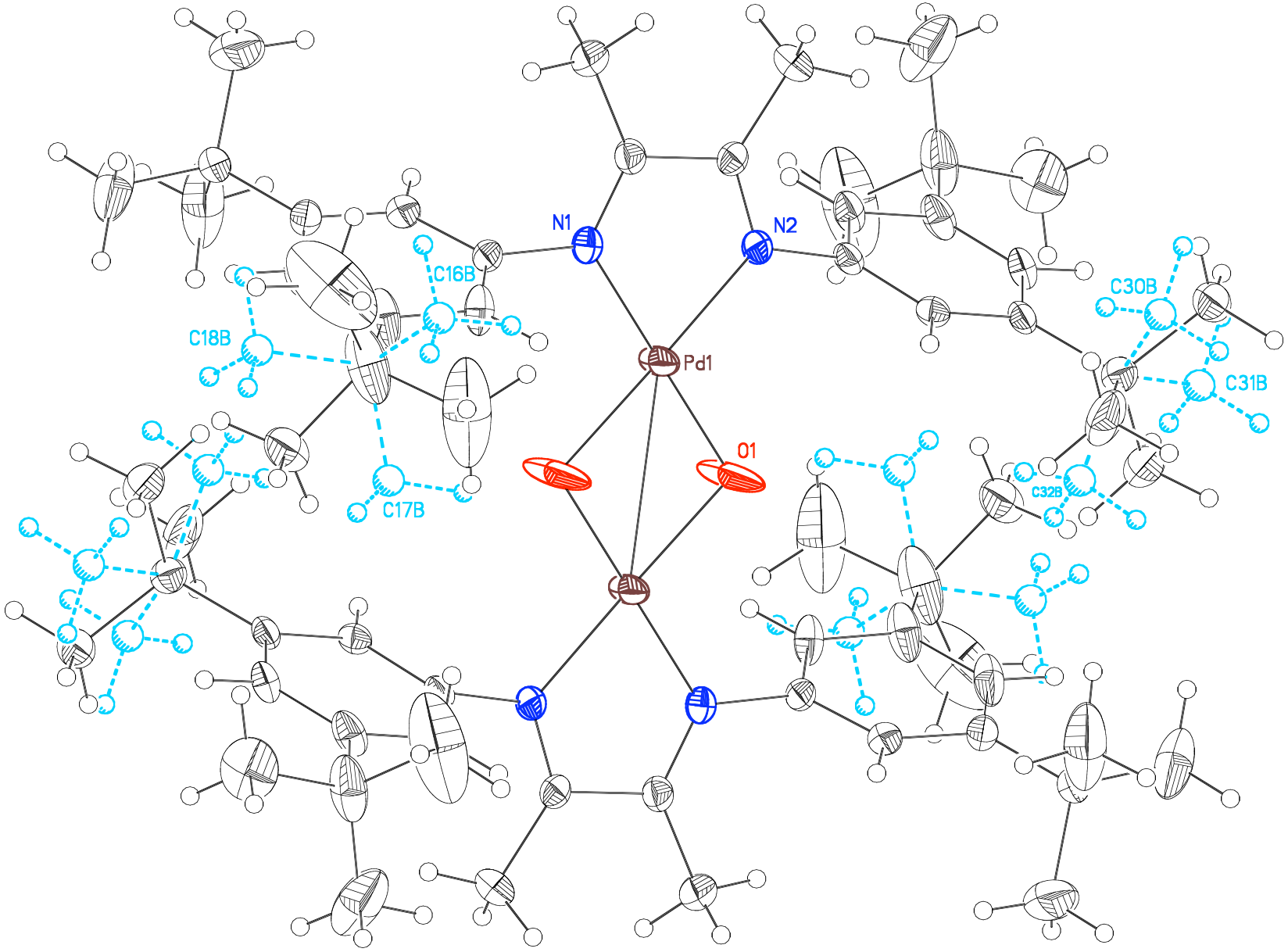

N1
N2
C16B
C18B
Pd1
C30B
C31B
O1
C17B
C32B

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1b. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Pd(1)	9361(1)	4016(1)	5310(1)	34(1)	1
O(1)	10047(4)	5713(2)	5835(2)	96(2)	1
N(1)	8616(3)	2353(2)	4797(2)	22(1)	1
N(2)	8744(3)	3721(2)	6421(2)	21(1)	1
C(1)	8089(3)	1872(3)	5347(2)	21(1)	1
C(2)	8207(3)	2684(3)	6318(2)	20(1)	1
C(3)	7414(4)	662(3)	5120(3)	33(1)	1
C(4)	7697(4)	2246(3)	7040(3)	31(1)	1
C(5)	8547(4)	1704(3)	3838(2)	21(1)	1
C(6)	7337(4)	1213(3)	3266(3)	27(1)	1
C(7)	7231(4)	546(3)	2338(3)	33(1)	1
C(8)	8381(4)	428(3)	2038(3)	34(1)	1
C(9)	9623(4)	950(3)	2605(2)	35(1)	1
C(10)	9689(4)	1602(3)	3523(2)	25(1)	1
C(11)	5867(5)	-11(4)	1733(3)	57(2)	1
C(12)	5015(6)	-797(6)	2153(4)	154(4)	1
C(13)	5931(5)	-606(4)	735(3)	57(2)	1
C(14)	5205(5)	861(5)	1729(3)	84(2)	1
C(15)	10761(4)	684(2)	2218(2)	57(2)	1
C(16A)	10580(6)	-571(4)	1932(4)	105(3)	0.764(7)
C(17A)	12029(3)	1306(6)	2923(3)	114(4)	0.764(7)
C(18A)	10962(4)	1009(4)	1360(3)	40(2)	0.764(7)
C(16B)	11448(11)	189(14)	2800(7)	47(6)	0.236(7)
C(17B)	11780(8)	1733(5)	2186(11)	157(17)	0.236(7)
C(18B)	10349(6)	-166(11)	1231(5)	380(40)	0.236(7)
C(19)	8828(4)	4586(3)	7287(2)	20(1)	1
C(20)	7664(4)	4741(3)	7530(2)	24(1)	1
C(21)	7696(4)	5539(3)	8388(3)	28(1)	1
C(22)	8893(4)	6131(3)	8957(2)	23(1)	1
C(23)	10085(4)	5994(3)	8712(2)	19(1)	1
C(24)	10026(3)	5204(3)	7861(2)	19(1)	1
C(25)	6405(4)	5670(4)	8662(3)	48(1)	1
C(26)	5601(4)	4587(4)	8750(3)	75(2)	1
C(27)	6595(4)	6637(4)	9582(3)	55(1)	1
C(28)	5675(5)	5951(6)	7913(4)	106(2)	1
C(29)	11394(3)	6701(3)	9386(2)	23(1)	1
C(30A)	11329(5)	6542(5)	10323(3)	36(2)	0.724(5)
C(31A)	11680(6)	7948(3)	9538(4)	41(2)	0.724(5)
C(32A)	12559(4)	6383(5)	9015(4)	47(2)	0.724(5)
C(30B)	11903(17)	5889(12)	9709(13)	58(6)	0.276(5)
C(31B)	11206(19)	7640(12)	10191(9)	74(7)	0.276(5)
C(32B)	12284(12)	7194(12)	8794(9)	36(4)	0.276(5)
B(1)	4710(8)	2274(6)	5333(5)	64(2)	1
F(1)	4711(3)	1819(3)	6034(3)	107(1)	1
F(2)	3441(5)	1967(6)	4984(4)	72(2)	0.635(8)
F(3)	5059(8)	3453(5)	5782(6)	142(4)	0.635(8)
F(4)	5499(9)	2057(9)	4843(7)	163(4)	0.635(8)

F(2B)	3745(14)	2675(11)	5127(9)	88(4)	0.365(8)
F(3B)	5950(10)	2893(10)	5384(7)	82(4)	0.365(8)
F(4B)	4662(10)	1326(7)	4445(5)	59(3)	0.365(8)

Table S3. Selected bond lengths [Å] and angles [°] for 1b.

Pd(1)-N(1)	1.982(3)	N(1)-Pd(1)-N(2)	79.96(12)
Pd(1)-N(2)	1.989(3)	N(1)-Pd(1)-O(1)	177.72(16)
Pd(1)-O(1)	2.018(3)	N(2)-Pd(1)-O(1)	99.21(12)
Pd(1)-O(1)#1	2.018(3)	N(1)-Pd(1)-O(1)#1	99.04(12)
Pd(1)-Pd(1)#1	3.0514(6)	N(2)-Pd(1)-O(1)#1	178.76(14)
O(1)-Pd(1)#1	2.018(3)	O(1)-Pd(1)-O(1)#1	81.77(13)
		N(1)-Pd(1)-Pd(1)#1	139.89(9)
		N(2)-Pd(1)-Pd(1)#1	140.08(8)
		O(1)-Pd(1)-Pd(1)#1	40.88(8)
		O(1)#1-Pd(1)-Pd(1)#1	40.89(8)
		Pd(1)-O(1)-Pd(1)#1	98.23(13)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+1

Table S4. Bond lengths [Å] and angles [°] for 1b.

Pd(1)-N(1)	1.982(3)	B(1)-F(1)	1.391(8)
Pd(1)-N(2)	1.989(3)	B(1)-F(3)	1.416(9)
Pd(1)-O(1)	2.018(3)	B(1)-F(4B)	1.522(11)
Pd(1)-O(1)#1	2.018(3)		
Pd(1)-Pd(1)#1	3.0514(6)	N(1)-Pd(1)-N(2)	79.96(12)
O(1)-Pd(1)#1	2.018(3)	N(1)-Pd(1)-O(1)	177.72(16)
N(1)-C(1)	1.283(4)	N(2)-Pd(1)-O(1)	99.21(12)
N(1)-C(5)	1.440(4)	N(1)-Pd(1)-O(1)#1	99.04(12)
N(2)-C(2)	1.281(4)	N(2)-Pd(1)-O(1)#1	178.76(14)
N(2)-C(19)	1.436(4)	O(1)-Pd(1)-O(1)#1	81.77(13)
C(1)-C(3)	1.472(5)	N(1)-Pd(1)-Pd(1)#1	139.89(9)
C(1)-C(2)	1.514(5)	N(2)-Pd(1)-Pd(1)#1	140.08(8)
C(2)-C(4)	1.478(5)	O(1)-Pd(1)-Pd(1)#1	40.88(8)
C(5)-C(6)	1.380(5)	O(1)#1-Pd(1)-Pd(1)#1	40.89(8)
C(5)-C(10)	1.380(5)	Pd(1)-O(1)-Pd(1)#1	98.23(13)
C(6)-C(7)	1.401(5)	C(1)-N(1)-C(5)	120.4(3)
C(7)-C(8)	1.385(6)	C(1)-N(1)-Pd(1)	116.5(2)
C(7)-C(11)	1.530(6)	C(5)-N(1)-Pd(1)	122.9(2)
C(8)-C(9)	1.403(5)	C(2)-N(2)-C(19)	120.0(3)
C(9)-C(10)	1.390(4)	C(2)-N(2)-Pd(1)	115.8(2)
C(9)-C(15)	1.482(6)	C(19)-N(2)-Pd(1)	124.1(2)
C(11)-C(13)	1.507(6)	N(1)-C(1)-C(3)	126.9(3)
C(11)-C(12)	1.520(6)	N(1)-C(1)-C(2)	113.4(3)
C(11)-C(14)	1.517(7)	C(3)-C(1)-C(2)	119.7(3)
C(15)-C(17A)	1.524(2)	N(2)-C(2)-C(4)	126.2(3)
C(15)-C(18A)	1.524(2)	N(2)-C(2)-C(1)	114.3(3)
C(15)-C(16B)	1.524(2)	C(4)-C(2)-C(1)	119.5(3)
C(15)-C(18B)	1.525(2)	C(6)-C(5)-C(10)	122.4(3)
C(15)-C(17B)	1.526(2)	C(6)-C(5)-N(1)	118.5(3)
C(15)-C(16A)	1.527(2)	C(10)-C(5)-N(1)	119.1(3)
C(19)-C(20)	1.385(5)	C(5)-C(6)-C(7)	119.9(4)
C(19)-C(24)	1.382(5)	C(8)-C(7)-C(6)	117.0(4)
C(20)-C(21)	1.398(5)	C(8)-C(7)-C(11)	124.7(4)
C(21)-C(22)	1.375(5)	C(6)-C(7)-C(11)	118.3(4)
C(21)-C(25)	1.522(5)	C(7)-C(8)-C(9)	123.7(4)
C(22)-C(23)	1.409(5)	C(10)-C(9)-C(8)	117.7(4)
C(23)-C(24)	1.379(4)	C(10)-C(9)-C(15)	123.9(3)
C(23)-C(29)	1.545(5)	C(8)-C(9)-C(15)	118.2(3)
C(25)-C(26)	1.504(7)	C(5)-C(10)-C(9)	119.3(4)
C(25)-C(27)	1.535(6)	C(13)-C(11)-C(7)	111.8(5)
C(25)-C(28)	1.547(6)	C(13)-C(11)-C(12)	112.3(5)
C(29)-C(30B)	1.525(2)	C(7)-C(11)-C(12)	108.8(4)
C(29)-C(31B)	1.525(2)	C(13)-C(11)-C(14)	106.5(4)
C(29)-C(32B)	1.525(2)	C(7)-C(11)-C(14)	110.8(4)
C(29)-C(32A)	1.525(2)	C(12)-C(11)-C(14)	106.6(6)
C(29)-C(30A)	1.525(2)	C(9)-C(15)-C(17A)	111.6(2)
C(29)-C(31A)	1.526(2)	C(9)-C(15)-C(18A)	111.7(2)
B(1)-F(4)	1.210(9)	C(17A)-C(15)-C(18A)	107.4(2)
B(1)-F(2)	1.331(9)	C(9)-C(15)-C(16B)	111.7(2)
B(1)-F(2B)	1.353(13)	C(17A)-C(15)-C(16B)	53.7(6)
B(1)-F(3B)	1.340(12)	C(18A)-C(15)-C(16B)	136.6(4)

C(9)-C(15)-C(18B)	111.6(2)	F(4)-B(1)-F(2)	121.5(9)
C(17A)-C(15)-C(18B)	136.7(4)	F(4)-B(1)-F(2B)	125.3(10)
C(18A)-C(15)-C(18B)	56.7(6)	F(2)-B(1)-F(2B)	36.8(5)
C(16B)-C(15)-C(18B)	107.3(2)	F(4)-B(1)-F(3B)	50.9(6)
C(9)-C(15)-C(17B)	111.5(2)	F(2)-B(1)-F(3B)	149.2(8)
C(17A)-C(15)-C(17B)	57.1(6)	F(2B)-B(1)-F(3B)	117.6(10)
C(18A)-C(15)-C(17B)	54.0(6)	F(4)-B(1)-F(1)	111.2(8)
C(16B)-C(15)-C(17B)	107.3(2)	F(2)-B(1)-F(1)	103.3(6)
C(18B)-C(15)-C(17B)	107.2(2)	F(2B)-B(1)-F(1)	122.0(8)
C(9)-C(15)-C(16A)	111.4(2)	F(3B)-B(1)-F(1)	107.0(7)
C(17A)-C(15)-C(16A)	107.2(2)	F(4)-B(1)-F(3)	109.7(8)
C(18A)-C(15)-C(16A)	107.2(2)	F(2)-B(1)-F(3)	103.7(7)
C(16B)-C(15)-C(16A)	57.0(6)	F(2B)-B(1)-F(3)	68.2(7)
C(18B)-C(15)-C(16A)	53.9(6)	F(3B)-B(1)-F(3)	62.4(6)
C(17B)-C(15)-C(16A)	137.0(4)	F(1)-B(1)-F(3)	106.3(7)
C(20)-C(19)-C(24)	122.2(3)	F(4)-B(1)-F(4B)	45.2(6)
C(20)-C(19)-N(2)	117.3(3)	F(2)-B(1)-F(4B)	81.3(6)
C(24)-C(19)-N(2)	120.5(3)	F(2B)-B(1)-F(4B)	105.0(8)
C(19)-C(20)-C(21)	119.1(3)	F(3B)-B(1)-F(4B)	95.9(8)
C(22)-C(21)-C(20)	118.0(3)	F(1)-B(1)-F(4B)	105.4(6)
C(22)-C(21)-C(25)	123.4(3)	F(3)-B(1)-F(4B)	145.7(8)
C(20)-C(21)-C(25)	118.6(4)		
C(21)-C(22)-C(23)	123.4(3)		
C(24)-C(23)-C(22)	117.4(3)		
C(24)-C(23)-C(29)	122.2(3)		
C(22)-C(23)-C(29)	120.4(3)		
C(19)-C(24)-C(23)	119.9(3)		
C(21)-C(25)-C(26)	108.4(4)		
C(21)-C(25)-C(27)	112.9(4)		
C(26)-C(25)-C(27)	109.0(4)		
C(21)-C(25)-C(28)	109.3(4)		
C(26)-C(25)-C(28)	110.8(4)		
C(27)-C(25)-C(28)	106.3(4)		
C(23)-C(29)-C(30B)	106.8(7)		
C(23)-C(29)-C(31B)	111.0(8)		
C(30B)-C(29)-C(31B)	112.6(10)		
C(23)-C(29)-C(32B)	104.4(6)		
C(30B)-C(29)-C(32B)	111.4(9)		
C(31B)-C(29)-C(32B)	110.4(10)		
C(23)-C(29)-C(32A)	112.3(3)		
C(30B)-C(29)-C(32A)	60.4(7)		
C(31B)-C(29)-C(32A)	136.1(8)		
C(32B)-C(29)-C(32A)	51.3(6)		
C(23)-C(29)-C(30A)	110.0(3)		
C(30B)-C(29)-C(30A)	53.6(7)		
C(31B)-C(29)-C(30A)	61.7(8)		
C(32B)-C(29)-C(30A)	145.2(7)		
C(32A)-C(29)-C(30A)	108.5(4)		
C(23)-C(29)-C(31A)	110.7(3)		
C(30B)-C(29)-C(31A)	142.3(8)		
C(31B)-C(29)-C(31A)	49.8(8)		
C(32B)-C(29)-C(31A)	62.2(6)		
C(32A)-C(29)-C(31A)	106.5(4)		
C(30A)-C(29)-C(31A)	108.6(4)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+1

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 1b. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	584(2)	157(1)	180(2)	4(1)	208(2)	-23(1)
O(1)	1970(40)	196(17)	400(20)	11(15)	730(20)	-150(20)
N(1)	261(19)	198(16)	154(16)	22(13)	29(14)	53(14)
N(2)	219(18)	215(16)	140(15)	31(12)	56(13)	37(14)
C(1)	240(20)	208(18)	181(19)	69(15)	4(16)	67(16)
C(2)	140(20)	240(19)	195(19)	72(15)	-7(15)	33(15)
C(3)	400(30)	230(20)	280(20)	86(17)	-9(19)	-10(18)
C(4)	370(30)	340(20)	250(20)	175(18)	68(19)	77(19)
C(5)	320(20)	116(16)	156(18)	24(14)	17(17)	31(16)
C(6)	230(20)	300(20)	230(20)	121(17)	0(18)	-11(17)
C(7)	450(30)	230(20)	210(20)	91(16)	-70(20)	-42(19)
C(8)	590(30)	240(20)	170(20)	17(16)	-50(20)	200(20)
C(9)	540(30)	390(20)	190(20)	36(17)	20(20)	340(20)
C(10)	300(20)	280(20)	177(19)	5(16)	-33(17)	194(18)
C(11)	650(30)	520(30)	260(20)	230(20)	-160(20)	-280(30)
C(12)	1330(50)	1600(60)	860(50)	860(50)	-590(40)	-1100(40)
C(13)	740(40)	380(30)	450(30)	-20(20)	-280(30)	240(30)
C(14)	430(40)	1490(60)	340(30)	-30(30)	20(30)	300(40)
C(15)	760(40)	870(40)	280(30)	120(20)	130(20)	640(30)
C(16A)	1660(70)	1320(60)	1030(60)	700(50)	890(50)	1320(60)
C(17A)	460(50)	2300(90)	420(40)	-30(50)	40(40)	660(50)
C(18A)	200(30)	660(40)	390(30)	320(30)	0(30)	80(30)
C(19)	250(20)	213(18)	130(17)	65(14)	71(16)	66(16)
C(20)	150(20)	420(20)	176(19)	113(17)	32(16)	110(18)
C(21)	290(20)	430(20)	175(19)	117(17)	107(18)	189(19)
C(22)	280(20)	300(20)	131(17)	70(15)	38(17)	127(18)
C(23)	250(20)	196(18)	122(17)	62(14)	46(16)	73(16)
C(24)	160(20)	233(18)	181(18)	82(15)	77(16)	58(16)
C(25)	310(30)	890(40)	210(20)	70(20)	100(20)	300(30)
C(26)	330(30)	840(40)	570(30)	-220(30)	210(30)	-90(30)
C(27)	430(30)	710(30)	520(30)	70(30)	270(20)	300(30)
C(28)	860(40)	2160(70)	510(40)	290(40)	230(30)	1170(50)
C(29)	230(20)	220(19)	230(20)	63(15)	52(17)	66(17)
C(30A)	230(30)	500(40)	290(30)	200(30)	-10(30)	-10(30)
C(31A)	420(40)	320(30)	380(40)	130(30)	-80(30)	-20(30)
C(32A)	210(40)	600(40)	350(40)	-20(30)	-20(30)	-10(30)
B(1)	550(50)	610(40)	690(50)	210(40)	70(40)	140(40)
F(1)	830(30)	1640(40)	850(30)	610(30)	60(20)	380(30)
F(2)	380(30)	670(40)	990(40)	380(40)	-270(30)	-10(30)
F(3)	1130(60)	810(50)	1690(70)	-30(40)	-610(50)	100(40)
F(4)	1150(70)	1840(80)	1860(80)	280(60)	860(60)	710(60)
F(2B)	940(80)	890(80)	1020(70)	440(60)	200(60)	510(70)
F(3B)	470(60)	960(70)	790(70)	240(50)	10(50)	-40(50)
F(4B)	790(70)	470(50)	420(50)	180(40)	90(40)	40(40)

VIII. X-ray structure determination for 2b

Crystallographic data for **2b** have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 690332.

Table S6. Crystal data and structure refinement for 2b.

Empirical formula	$[C_{32}H_{52}N_2O_2Pd]^{+2}\ 2(BF_4)^-$
Formula weight	776.78
Crystallization Solvent	Dichloromethane
Crystal Habit	Plate
Crystal size	0.18 x 0.17 x 0.07 mm^3
Crystal color	Pale yellow

Data Collection

Type of diffractometer	Bruker KAPPA APEX II
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 9055 reflections used in lattice determination	2.51 to 40.91°
Unit cell dimensions	a = 32.1962(14) Å b = 11.3418(5) Å β= 95.799(3)° c = 10.0182(5) Å
Volume	3639.6(3) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	C2
Density (calculated)	1.418 Mg/m^3
F(000)	1608
Data collection program	Bruker APEX2 v2.1-0
θ range for data collection	1.90 to 41.45°
Completeness to θ = 41.45°	96.4 %
Index ranges	$-59 \le h \le 58, -20 \le k \le 20, -17 \le l \le 18$
Data collection scan type	ω scans; 29 settings
Data reduction program	Bruker SAINT-Plus v7.34A
Reflections collected	108406
Independent reflections	22782 [R_{int}= 0.0495]
Absorption coefficient	0.581 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9604 and 0.9026

Table S6 (cont.)

Structure solution and Refinement

Structure solution program	SIR92 – (A. Altomare, et al., *J. Appl. Crystallogr.* **1993**, 26, 343-350.)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	22782 / 1 / 632
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.814
Final R indices [I>2σ(I), 19272 reflections]	R1 = 0.0363, *w*R2 = 0.0590
R indices (all data)	R1 = 0.0479, *w*R2 = 0.0595
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Absolute structure determination	Racemic twin
Absolute structure parameter	0.00
Largest diff. peak and hole	4.468 and -1.136 e.Å^{-3}

Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

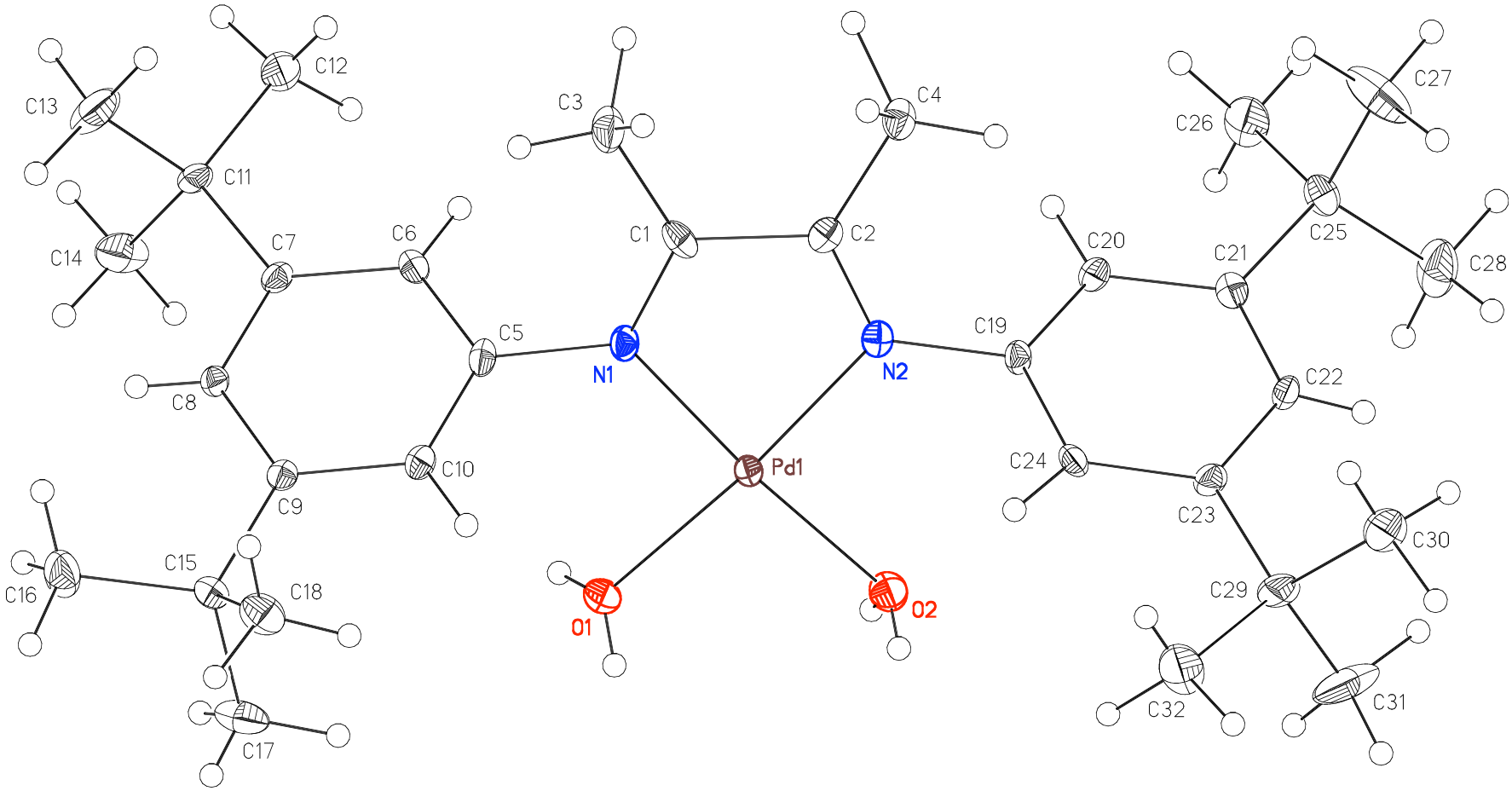

C12
C13
C11
C14
C7
C6
C3
C1
C2
C4
C5
N1
N2
C19
C20
C21
C25
C27
C26
C28
C8
C10
Pd1
C22
C24
C9
C23
C30
C15
C16
C18
C29
O1
O2
C32
C31
C17

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 2b. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Pd(1)	7430(1)	5540(1)	1605(1)	10(1)
O(1)	7781(1)	6413(1)	315(1)	16(1)
O(2)	6913(1)	5728(1)	239(1)	16(1)
N(1)	7904(1)	5249(1)	2974(1)	11(1)
N(2)	7135(1)	4661(1)	2942(1)	11(1)
C(1)	7813(1)	4634(1)	3995(2)	13(1)
C(2)	7373(1)	4269(1)	3964(2)	11(1)
C(3)	8115(1)	4304(2)	5162(2)	20(1)
C(4)	7236(1)	3530(2)	5051(2)	15(1)
C(5)	8326(1)	5586(2)	2785(1)	12(1)
C(6)	8611(1)	4698(1)	2627(2)	12(1)
C(7)	9020(1)	4993(2)	2448(2)	11(1)
C(8)	9125(1)	6186(2)	2431(2)	10(1)
C(9)	8841(1)	7092(1)	2561(2)	10(1)
C(10)	8430(1)	6767(2)	2728(2)	11(1)
C(11)	9353(1)	4049(1)	2294(2)	13(1)
C(12)	9180(1)	2801(2)	2356(2)	21(1)
C(13)	9705(1)	4205(2)	3432(2)	27(1)
C(14)	9525(1)	4209(2)	937(2)	25(1)
C(15)	8961(1)	8399(1)	2460(2)	13(1)
C(16)	9430(1)	8586(2)	2588(3)	24(1)
C(17)	8775(1)	8842(2)	1075(2)	23(1)
C(18)	8780(1)	9125(2)	3543(2)	19(1)
C(19)	6693(1)	4470(1)	2785(2)	10(1)
C(20)	6530(1)	3344(1)	2591(2)	11(1)
C(21)	6098(1)	3175(2)	2506(2)	12(1)
C(22)	5848(1)	4168(2)	2588(2)	12(1)
C(23)	6006(1)	5316(1)	2744(2)	13(1)
C(24)	6438(1)	5453(2)	2840(2)	12(1)
C(25)	5902(1)	1944(1)	2402(2)	15(1)
C(26)	6196(1)	1043(2)	1877(3)	25(1)
C(27)	5803(1)	1582(2)	3809(2)	35(1)
C(28)	5497(1)	1934(2)	1470(2)	27(1)
C(29)	5706(1)	6352(2)	2803(2)	18(1)
C(30)	5423(1)	6143(2)	3932(2)	22(1)
C(31)	5433(1)	6423(2)	1461(2)	35(1)
C(32)	5935(1)	7516(2)	3065(3)	35(1)
B(1)	7034(1)	8538(2)	980(2)	20(1)
F(1)	7177(1)	7970(1)	2166(1)	30(1)
F(2)	6670(1)	7975(1)	445(1)	35(1)
F(3)	6949(1)	9713(1)	1229(1)	32(1)
F(4)	7334(1)	8464(1)	88(1)	36(1)
B(2)	7810(1)	1441(2)	3010(2)	21(1)
F(5)	7739(1)	1111(1)	4283(1)	46(1)
F(6)	7473(1)	2074(1)	2420(1)	46(1)
F(7)	8156(1)	2126(1)	3049(2)	69(1)
F(8)	7871(1)	433(1)	2236(1)	24(1)

Table S8. Selected bond lengths [Å] and angles [°] for 2b.

Pd(1)-N(1)	1.9730(13)	N(1)-Pd(1)-N(2)	80.53(5)
Pd(1)-N(2)	1.9858(13)	N(1)-Pd(1)-O(2)	175.38(5)
Pd(1)-O(2)	2.0557(13)	N(2)-Pd(1)-O(2)	95.26(5)
Pd(1)-O(1)	2.0565(12)	N(1)-Pd(1)-O(1)	94.68(5)
		N(2)-Pd(1)-O(1)	175.14(6)
		O(2)-Pd(1)-O(1)	89.50(5)

Table S9. Bond lengths [Å] and angles [°] for 2b.

Pd(1)-N(1)	1.9730(13)	C(18)-H(18A)	0.83(2)
Pd(1)-N(2)	1.9858(13)	C(18)-H(18B)	0.906(18)
Pd(1)-O(2)	2.0557(13)	C(18)-H(18C)	0.92(2)
Pd(1)-O(1)	2.0565(12)	C(19)-C(24)	1.388(3)
O(1)-H(1A)	0.70(2)	C(19)-C(20)	1.387(2)
O(1)-H(1B)	0.79(3)	C(20)-C(21)	1.399(2)
O(2)-H(2A)	0.73(2)	C(20)-H(20)	0.955(16)
O(2)-H(2B)	0.70(2)	C(21)-C(22)	1.390(2)
N(1)-C(1)	1.2951(19)	C(21)-C(25)	1.531(2)
N(1)-C(5)	1.4430(16)	C(22)-C(23)	1.400(2)
N(2)-C(2)	1.293(2)	C(22)-H(22)	0.808(17)
N(2)-C(19)	1.4344(18)	C(23)-C(24)	1.3936(18)
C(1)-C(3)	1.490(2)	C(23)-C(29)	1.525(2)
C(1)-C(2)	1.475(2)	C(24)-H(24)	0.956(14)
C(2)-C(4)	1.476(2)	C(25)-C(26)	1.520(3)
C(3)-H(3A)	1.05(2)	C(25)-C(28)	1.526(3)
C(3)-H(3B)	0.97(2)	C(25)-C(27)	1.533(3)
C(3)-H(3C)	0.91(2)	C(26)-H(26A)	0.92(2)
C(4)-H(4A)	0.987(18)	C(26)-H(26B)	0.983(18)
C(4)-H(4B)	0.95(2)	C(26)-H(26C)	0.957(19)
C(4)-H(4C)	1.12(3)	C(27)-H(27A)	0.92(2)
C(5)-C(10)	1.383(3)	C(27)-H(27B)	1.01(2)
C(5)-C(6)	1.384(3)	C(27)-H(27C)	0.98(3)
C(6)-C(7)	1.387(2)	C(28)-H(28A)	0.96(2)
C(6)-H(6)	0.841(14)	C(28)-H(28B)	0.95(2)
C(7)-C(8)	1.395(2)	C(28)-H(28C)	1.043(19)
C(7)-C(11)	1.534(2)	C(29)-C(32)	1.522(3)
C(8)-C(9)	1.390(2)	C(29)-C(31)	1.532(3)
C(8)-H(8)	0.794(18)	C(29)-C(30)	1.541(2)
C(9)-C(10)	1.400(2)	C(30)-H(30A)	0.87(2)
C(9)-C(15)	1.538(2)	C(30)-H(30B)	0.89(2)
C(10)-H(10)	0.919(16)	C(30)-H(30C)	0.96(2)
C(11)-C(12)	1.525(2)	C(31)-H(31A)	1.12(3)
C(11)-C(14)	1.529(2)	C(31)-H(31B)	0.80(2)
C(11)-C(13)	1.535(3)	C(31)-H(31C)	0.88(3)
C(12)-H(12A)	0.840(18)	C(32)-H(32A)	0.88(3)
C(12)-H(12B)	1.00(3)	C(32)-H(32B)	0.996(18)
C(12)-H(12C)	1.009(15)	C(32)-H(32C)	0.80(2)
C(13)-H(13A)	1.008(19)	B(1)-F(1)	1.389(2)
C(13)-H(13B)	0.88(2)	B(1)-F(3)	1.388(2)
C(13)-H(13C)	0.97(2)	B(1)-F(4)	1.384(2)
C(14)-H(14A)	1.01(2)	B(1)-F(2)	1.394(2)
C(14)-H(14B)	0.92(2)	B(2)-F(7)	1.356(2)
C(14)-H(14C)	0.92(2)	B(2)-F(5)	1.370(2)
C(15)-C(16)	1.519(2)	B(2)-F(6)	1.382(2)
C(15)-C(18)	1.523(2)	B(2)-F(8)	1.406(2)
C(15)-C(17)	1.539(3)		
C(16)-H(16A)	0.91(2)	N(1)-Pd(1)-N(2)	80.53(5)
C(16)-H(16B)	0.82(2)	N(1)-Pd(1)-O(2)	175.38(5)
C(16)-H(16C)	0.97(2)	N(2)-Pd(1)-O(2)	95.26(5)
C(17)-H(17A)	0.72(2)	N(1)-Pd(1)-O(1)	94.68(5)
C(17)-H(17B)	0.99(2)	N(2)-Pd(1)-O(1)	175.14(6)
C(17)-H(17C)	1.05(2)	O(2)-Pd(1)-O(1)	89.50(5)

Pd(1)-O(1)-H(1A)	118.7(17)	C(11)-C(12)-H(12B)	107.8(16)
Pd(1)-O(1)-H(1B)	118(2)	H(12A)-C(12)-H(12B)	115(2)
H(1A)-O(1)-H(1B)	113(3)	C(11)-C(12)-H(12C)	112.7(8)
Pd(1)-O(2)-H(2A)	112.6(15)	H(12A)-C(12)-H(12C)	103.0(15)
Pd(1)-O(2)-H(2B)	111.2(19)	H(12B)-C(12)-H(12C)	105.2(18)
H(2A)-O(2)-H(2B)	110(3)	C(11)-C(13)-H(13A)	115.4(12)
C(1)-N(1)-C(5)	122.40(14)	C(11)-C(13)-H(13B)	110.0(14)
C(1)-N(1)-Pd(1)	114.83(10)	H(13A)-C(13)-H(13B)	112.6(16)
C(5)-N(1)-Pd(1)	122.47(10)	C(11)-C(13)-H(13C)	107.3(13)
C(2)-N(2)-C(19)	122.43(13)	H(13A)-C(13)-H(13C)	108.1(18)
C(2)-N(2)-Pd(1)	114.98(10)	H(13B)-C(13)-H(13C)	102.6(18)
C(19)-N(2)-Pd(1)	122.59(10)	C(11)-C(14)-H(14A)	118.2(13)
N(1)-C(1)-C(3)	125.08(14)	C(11)-C(14)-H(14B)	107.0(13)
N(1)-C(1)-C(2)	115.25(14)	H(14A)-C(14)-H(14B)	115.8(18)
C(3)-C(1)-C(2)	119.67(14)	C(11)-C(14)-H(14C)	112.9(16)
N(2)-C(2)-C(4)	125.60(14)	H(14A)-C(14)-H(14C)	97.4(19)
N(2)-C(2)-C(1)	114.22(14)	H(14B)-C(14)-H(14C)	104.5(18)
C(4)-C(2)-C(1)	120.17(14)	C(16)-C(15)-C(18)	108.22(16)
C(1)-C(3)-H(3A)	110.7(11)	C(16)-C(15)-C(9)	112.58(14)
C(1)-C(3)-H(3B)	106.4(12)	C(18)-C(15)-C(9)	110.98(13)
H(3A)-C(3)-H(3B)	110.5(16)	C(16)-C(15)-C(17)	108.84(16)
C(1)-C(3)-H(3C)	110.8(15)	C(18)-C(15)-C(17)	108.90(15)
H(3A)-C(3)-H(3C)	110.1(17)	C(9)-C(15)-C(17)	107.25(15)
H(3B)-C(3)-H(3C)	108.2(18)	C(15)-C(16)-H(16A)	106.2(12)
C(2)-C(4)-H(4A)	112.0(11)	C(15)-C(16)-H(16B)	117.2(17)
C(2)-C(4)-H(4B)	103.2(12)	H(16A)-C(16)-H(16B)	112(2)
H(4A)-C(4)-H(4B)	107.8(16)	C(15)-C(16)-H(16C)	109.4(11)
C(2)-C(4)-H(4C)	111.9(14)	H(16A)-C(16)-H(16C)	111.0(17)
H(4A)-C(4)-H(4C)	124.5(18)	H(16B)-C(16)-H(16C)	101.2(19)
H(4B)-C(4)-H(4C)	93(2)	C(15)-C(17)-H(17A)	112(2)
C(10)-C(5)-C(6)	122.29(13)	C(15)-C(17)-H(17B)	112.9(13)
C(10)-C(5)-N(1)	119.81(16)	H(17A)-C(17)-H(17B)	107(2)
C(6)-C(5)-N(1)	117.9(2)	C(15)-C(17)-H(17C)	112.7(11)
C(5)-C(6)-C(7)	119.27(16)	H(17A)-C(17)-H(17C)	103(2)
C(5)-C(6)-H(6)	116.4(9)	H(17B)-C(17)-H(17C)	109.2(16)
C(7)-C(6)-H(6)	124.3(9)	C(15)-C(18)-H(18A)	109.8(13)
C(6)-C(7)-C(8)	118.02(14)	C(15)-C(18)-H(18B)	106.7(12)
C(6)-C(7)-C(11)	121.78(16)	H(18A)-C(18)-H(18B)	113.5(17)
C(8)-C(7)-C(11)	120.20(15)	C(15)-C(18)-H(18C)	112.7(12)
C(9)-C(8)-C(7)	123.57(14)	H(18A)-C(18)-H(18C)	101.9(18)
C(9)-C(8)-H(8)	117.8(14)	H(18B)-C(18)-H(18C)	112.3(16)
C(7)-C(8)-H(8)	118.6(14)	C(24)-C(19)-C(20)	121.96(13)
C(8)-C(9)-C(10)	117.15(15)	C(24)-C(19)-N(2)	117.29(14)
C(8)-C(9)-C(15)	122.26(13)	C(20)-C(19)-N(2)	120.75(13)
C(10)-C(9)-C(15)	120.53(13)	C(19)-C(20)-C(21)	119.61(14)
C(5)-C(10)-C(9)	119.65(14)	C(19)-C(20)-H(20)	119.7(10)
C(5)-C(10)-H(10)	122.4(10)	C(21)-C(20)-H(20)	120.7(10)
C(9)-C(10)-H(10)	118.0(10)	C(22)-C(21)-C(20)	117.54(15)
C(12)-C(11)-C(14)	108.25(16)	C(22)-C(21)-C(25)	120.52(14)
C(12)-C(11)-C(7)	112.41(13)	C(20)-C(21)-C(25)	121.87(15)
C(14)-C(11)-C(7)	109.03(14)	C(21)-C(22)-C(23)	123.68(14)
C(12)-C(11)-C(13)	108.80(15)	C(21)-C(22)-H(22)	123.4(14)
C(14)-C(11)-C(13)	109.92(15)	C(23)-C(22)-H(22)	112.7(14)
C(7)-C(11)-C(13)	108.43(15)	C(24)-C(23)-C(22)	117.41(15)
C(11)-C(12)-H(12A)	113.2(13)	C(24)-C(23)-C(29)	122.83(16)

C(22)-C(23)-C(29)	119.76(13)	F(1)-B(1)-F(2)	108.00(15)
C(19)-C(24)-C(23)	119.75(19)	F(3)-B(1)-F(2)	109.57(15)
C(19)-C(24)-H(24)	116.3(8)	F(4)-B(1)-F(2)	109.86(16)
C(23)-C(24)-H(24)	123.7(8)	F(7)-B(2)-F(5)	110.08(18)
C(26)-C(25)-C(28)	107.84(16)	F(7)-B(2)-F(6)	108.78(18)
C(26)-C(25)-C(21)	111.82(14)	F(5)-B(2)-F(6)	110.01(15)
C(28)-C(25)-C(21)	111.62(15)	F(7)-B(2)-F(8)	108.80(16)
C(26)-C(25)-C(27)	109.43(18)	F(5)-B(2)-F(8)	109.67(16)
C(28)-C(25)-C(27)	108.39(16)	F(6)-B(2)-F(8)	109.48(16)
C(21)-C(25)-C(27)	107.69(15)		
C(25)-C(26)-H(26A)	113.8(12)		
C(25)-C(26)-H(26B)	109.8(10)		
H(26A)-C(26)-H(26B)	103.0(16)		
C(25)-C(26)-H(26C)	112.1(11)		
H(26A)-C(26)-H(26C)	101.7(18)		
H(26B)-C(26)-H(26C)	115.9(14)		
C(25)-C(27)-H(27A)	112.5(12)		
C(25)-C(27)-H(27B)	111.2(12)		
H(27A)-C(27)-H(27B)	105.4(16)		
C(25)-C(27)-H(27C)	107.6(16)		
H(27A)-C(27)-H(27C)	108(2)		
H(27B)-C(27)-H(27C)	113(2)		
C(25)-C(28)-H(28A)	109.3(13)		
C(25)-C(28)-H(28B)	111.6(15)		
H(28A)-C(28)-H(28B)	106.8(19)		
C(25)-C(28)-H(28C)	109.9(11)		
H(28A)-C(28)-H(28C)	111.8(17)		
H(28B)-C(28)-H(28C)	107.3(17)		
C(32)-C(29)-C(23)	112.18(14)		
C(32)-C(29)-C(31)	109.31(19)		
C(23)-C(29)-C(31)	108.41(15)		
C(32)-C(29)-C(30)	108.57(17)		
C(23)-C(29)-C(30)	109.49(14)		
C(31)-C(29)-C(30)	108.82(16)		
C(29)-C(30)-H(30A)	109.9(12)		
C(29)-C(30)-H(30B)	110.2(10)		
H(30A)-C(30)-H(30B)	111.0(17)		
C(29)-C(30)-H(30C)	109.5(12)		
H(30A)-C(30)-H(30C)	116.2(18)		
H(30B)-C(30)-H(30C)	99.7(17)		
C(29)-C(31)-H(31A)	112.4(12)		
C(29)-C(31)-H(31B)	112.4(16)		
H(31A)-C(31)-H(31B)	111.1(19)		
C(29)-C(31)-H(31C)	111.4(18)		
H(31A)-C(31)-H(31C)	113(2)		
H(31B)-C(31)-H(31C)	96(2)		
C(29)-C(32)-H(32A)	103.8(16)		
C(29)-C(32)-H(32B)	116.1(11)		
H(32A)-C(32)-H(32B)	113.8(19)		
C(29)-C(32)-H(32C)	106.7(17)		
H(32A)-C(32)-H(32C)	111(2)		
H(32B)-C(32)-H(32C)	105.1(19)		
F(1)-B(1)-F(3)	110.24(16)		
F(1)-B(1)-F(4)	109.37(15)		
F(3)-B(1)-F(4)	109.78(15)		

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 2b. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	85(1)	103(1)	102(1)	8(1)	14(1)	-8(1)
O(1)	152(5)	184(7)	151(7)	58(6)	24(5)	-7(5)
O(2)	159(5)	187(10)	134(6)	14(6)	2(4)	-22(5)
N(1)	84(5)	125(7)	133(7)	-4(5)	35(4)	5(4)
N(2)	101(5)	110(6)	116(7)	-30(5)	19(5)	0(5)
C(1)	164(7)	98(7)	136(8)	-18(6)	76(6)	-28(5)
C(2)	120(6)	111(7)	112(8)	-33(6)	14(5)	22(5)
C(3)	120(7)	322(11)	166(9)	51(8)	-9(6)	-49(7)
C(4)	119(6)	220(9)	105(8)	0(7)	29(6)	-2(6)
C(5)	75(4)	168(7)	114(6)	-4(11)	15(4)	-3(9)
C(6)	111(6)	115(7)	140(8)	11(6)	26(6)	-18(5)
C(7)	95(7)	133(8)	100(8)	14(6)	19(6)	32(6)
C(8)	85(7)	125(8)	101(8)	19(6)	22(6)	7(6)
C(9)	98(6)	122(7)	73(7)	5(6)	7(5)	5(5)
C(10)	95(6)	128(8)	119(8)	-8(6)	17(5)	15(6)
C(11)	116(6)	114(7)	163(9)	27(6)	25(6)	48(5)
C(12)	162(8)	127(8)	355(12)	25(8)	66(8)	41(6)
C(13)	198(8)	228(10)	364(13)	-10(9)	-74(8)	92(8)
C(14)	299(9)	203(9)	276(11)	60(8)	169(8)	120(8)
C(15)	139(7)	100(7)	159(9)	16(6)	18(6)	-16(6)
C(16)	159(8)	136(9)	440(15)	-3(9)	68(9)	-19(7)
C(17)	337(10)	163(9)	190(11)	68(8)	2(8)	-15(8)
C(18)	239(8)	133(8)	206(11)	-21(8)	40(7)	-20(7)
C(19)	79(5)	111(7)	128(8)	-8(6)	34(5)	3(5)
C(20)	98(6)	119(7)	125(8)	-11(6)	15(5)	19(5)
C(21)	121(6)	138(8)	95(8)	-11(6)	8(6)	-19(6)
C(22)	71(6)	154(8)	133(8)	16(7)	1(5)	9(6)
C(23)	110(5)	141(10)	143(7)	25(6)	34(5)	38(5)
C(24)	109(5)	87(8)	178(7)	18(8)	49(4)	-14(7)
C(25)	160(7)	130(7)	162(9)	-30(6)	17(6)	-47(6)
C(26)	222(9)	118(8)	409(14)	-69(9)	18(9)	-21(7)
C(27)	575(15)	227(11)	269(13)	-14(9)	123(11)	-193(11)
C(28)	179(8)	219(10)	402(14)	-106(10)	-14(8)	-46(7)
C(29)	174(7)	126(8)	259(10)	37(7)	63(7)	79(6)
C(30)	189(8)	190(9)	280(12)	9(8)	88(8)	67(7)
C(31)	369(12)	407(14)	280(13)	128(11)	42(10)	267(11)
C(32)	234(10)	123(9)	720(20)	44(11)	175(12)	50(8)
B(1)	260(9)	165(9)	167(11)	2(8)	46(8)	30(7)
F(1)	492(7)	209(6)	193(6)	-36(5)	5(5)	60(5)
F(2)	328(6)	269(6)	442(8)	-25(6)	-72(5)	47(5)
F(3)	406(6)	163(5)	428(8)	22(5)	225(6)	64(5)
F(4)	499(7)	233(6)	386(8)	43(6)	270(6)	90(5)
B(2)	287(10)	169(9)	165(11)	-4(8)	28(8)	2(8)
F(5)	997(11)	221(6)	208(7)	74(5)	216(7)	158(6)
F(6)	653(9)	475(8)	231(7)	-80(6)	-59(6)	351(7)
F(7)	598(10)	450(9)	1045(15)	-98(9)	191(10)	-338(7)
F(8)	327(5)	230(6)	184(5)	-7(6)	55(4)	89(6)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 2b.

	x	y	z	U_{iso}
H(1A)	7690(6)	6890(20)	-60(20)	20(6)
H(1B)	7935(9)	6040(30)	-80(30)	87(12)
H(2A)	6954(5)	5570(30)	-440(20)	28(5)
H(2B)	6834(6)	6300(20)	250(20)	26(7)
H(3A)	8139(6)	3382(19)	5250(20)	31(6)
H(3B)	8007(6)	4639(18)	5950(20)	29(6)
H(3C)	8371(7)	4630(20)	5080(20)	40(6)
H(4A)	6928(6)	3483(17)	5011(19)	23(5)
H(4B)	7333(6)	3955(19)	5840(20)	30(6)
H(4C)	7453(10)	2770(30)	5300(30)	82(10)
H(6)	8520(4)	4002(13)	2635(15)	-15(3)
H(8)	9360(6)	6362(17)	2353(19)	17(5)
H(10)	8237(5)	7358(14)	2794(16)	5(4)
H(12A)	9074(5)	2659(16)	3073(19)	9(5)
H(12B)	9405(9)	2240(20)	2150(30)	58(9)
H(12C)	8941(4)	2649(13)	1645(16)	-9(3)
H(13A)	9834(6)	5016(16)	3510(20)	29(6)
H(13B)	9892(6)	3648(18)	3390(20)	26(5)
H(13C)	9589(6)	4030(19)	4270(20)	35(6)
H(14A)	9320(7)	4260(20)	110(30)	41(7)
H(14B)	9737(6)	3672(18)	900(20)	28(5)
H(14C)	9650(7)	4930(20)	850(30)	48(7)
H(16A)	9471(6)	9376(18)	2570(20)	21(5)
H(16B)	9563(7)	8240(20)	2050(20)	39(7)
H(16C)	9554(6)	8247(17)	3430(20)	18(5)
H(17A)	8820(7)	9450(20)	980(20)	31(7)
H(17B)	8468(7)	8749(18)	930(20)	35(6)
H(17C)	8911(6)	8436(17)	280(20)	26(5)
H(18A)	8872(5)	8880(16)	4290(20)	13(5)
H(18B)	8499(6)	9076(15)	3382(19)	15(5)
H(18C)	8873(6)	9889(17)	3570(20)	24(5)
H(20)	6714(5)	2692(15)	2521(17)	9(4)
H(22)	5596(6)	4150(16)	2486(19)	16(5)
H(24)	6577(4)	6190(13)	3025(15)	-10(3)
H(26A)	6086(6)	290(20)	1800(20)	33(7)
H(26B)	6443(5)	943(14)	2528(18)	17(5)
H(26C)	6250(5)	1205(16)	970(20)	17(5)
H(27A)	5693(6)	830(20)	3830(20)	36(7)
H(27B)	5585(7)	2114(19)	4140(20)	33(6)
H(27C)	6065(8)	1590(20)	4390(30)	66(9)
H(28A)	5550(7)	2223(19)	600(20)	34(6)
H(28B)	5293(7)	2440(20)	1790(20)	47(7)
H(28C)	5372(6)	1085(17)	1420(20)	31(6)
H(30A)	5575(6)	6057(16)	4700(20)	20(5)
H(30B)	5263(5)	5520(20)	3747(16)	17(4)
H(30C)	5212(6)	6748(17)	3900(20)	28(5)
H(31A)	5258(6)	5590(30)	1220(20)	46(6)
H(31B)	5562(6)	6618(19)	860(20)	28(6)
H(31C)	5269(8)	7050(20)	1430(30)	53(8)

H(32A)	5733(8)	8030(20)	3150(30)	56(8)
H(32B)	6127(6)	7754(16)	2393(19)	-1(5)
H(32C)	6082(7)	7440(20)	3750(20)	34(8)

Table S12. Hydrogen bonds for 2b [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...F(4)	0.70(2)	2.14(2)	2.7327(19)	143(2)
O(1)-H(1A)...F(6)#1	0.70(2)	2.38(2)	2.8786(18)	130(2)
O(1)-H(1B)...F(3)#2	0.79(3)	1.95(3)	2.6718(18)	151(3)
O(2)-H(2A)...F(8)#1	0.73(2)	1.94(2)	2.6634(17)	168(3)
O(2)-H(2B)...F(2)	0.70(2)	1.99(2)	2.6806(19)	173(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/2,y+1/2,-z
#2 -x+3/2,y-1/2,-z

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